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Characterization of the minimum energy path for the reaction of singlet methylene with N_2: The role of singlet methylene in prompt NO

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We report calculations of the minimum energy pathways connecting $^1CH_2+N_2$ to diazomethane and diazirine, for the rearrangement of diazirine to diazomethane, for the dissociation of diazirine to HCN_2+H, and of diazomethane to CH_2N+N. The calculations use complete active space self-consistent field (CASSCF) derivative methods to characterize the stationary points and internally contracted configuration interaction (ICCI) to determine the energetics. The calculations suggest a potential new source of prompt NO from the reaction of $^1CH_2$ with N_2 to give diazirine, and subsequent reaction of diazirine with hydrogen abstracters to form doublet HCN_2, which leads to HCN+N(^{4}S) on the previously studied CH+N_2 surface. The calculations also predict accurate 0 K heats of formation of 77.7 kcal/mol and 68.0 kcal/mol for diazirine and diazomethane, respectively. © *1995 American Institute of Physics.*

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I. INTRODUCTION

The reaction of singlet methylene ($^1CH_2$) with N_2 along with the reaction of CH($^2\Pi$) with N_2, which was previously studied by Walch,[1] are potentially important in the formation of "prompt" NO.[2] While triplet methylene is known to be important in some of the reactions leading to prompt NO formation,[2] the role of singlet methylene has not been considered previously. There have been several previous studies of the CH_2N_2 surface. An early study of the ground state and some of the low-lying excited states of diazomethane, at the ground state geometry, was carried out by Walch and Goddard.[3] More recent work has been carried out by Boldyrev, Schleyer, Higgins, Thomson, and Kramarenko[4] (BSHTK) who studied the diazirine and diazomethane minima and several saddle points on the CH_2N_2 as well as the $CHFN_2$ and CF_2N_2 potential energy surfaces. Guimon, Khayar, Gracian, Begtrup, and Pfister Guillouzo[5] (GKGBP), as part of a study on the decomposition of tetrazole, also reported a number of stationary points on the CH_2N_2 surface, including a saddle point connecting diazirine and diazomethane. These studies were carried out at a lower level of theory than that used in the present study and did not provide sufficiently detailed information for combustion modelling studies. In this paper we report a detailed study of the pathways for addition of $^1CH_2$ to N_2 to give diazomethane and diazirine and the pathway for rearrangement of diazirine to diazomethane. Calculations with extended basis sets are also reported which lead to accurate heats of formation for diazirine and diazomethane.

In Sec. II we discuss qualitative features of the reactions considered here. Section III contains the technical details of the calculations, Sec. IV contains the results, and Sec. V concludes the paper.

II. QUALITATIVE FEATURES

Figure 1 shows the qualitative features of the orbitals for the reaction of $^1CH_2$ with N_2 via a pathway in which the CH_2 attacks the π bond of N_2. In the $^1A_1$ ground state of methylene ($^1CH_2$) there is a substantial near degeneracy effect between the C 2*s* lone pair and the empty C 2*p* orbital of a'' symmetry. This leads to a pair of singlet coupled *sp* hybrid orbitals directed above and below the molecular plane, as indicated in Fig. 1(a). In the addition of $^1CH_2$ to N_2, two bond pairs undergo major changes. These are the two electrons in the CH_2 C 2*s* pair discussed earlier and the in plane π orbital of N_2. By analogy to the reaction of CH($^2\Pi$) with N_2 (Ref. 1) and the reaction of CH($^2\Pi$) with H_2 (Ref. 6), the addition of $^1CH_2$ to N_2 occurs via a pathway, as shown in Fig. 1(a), in which the CH and N_2 approach each other in a

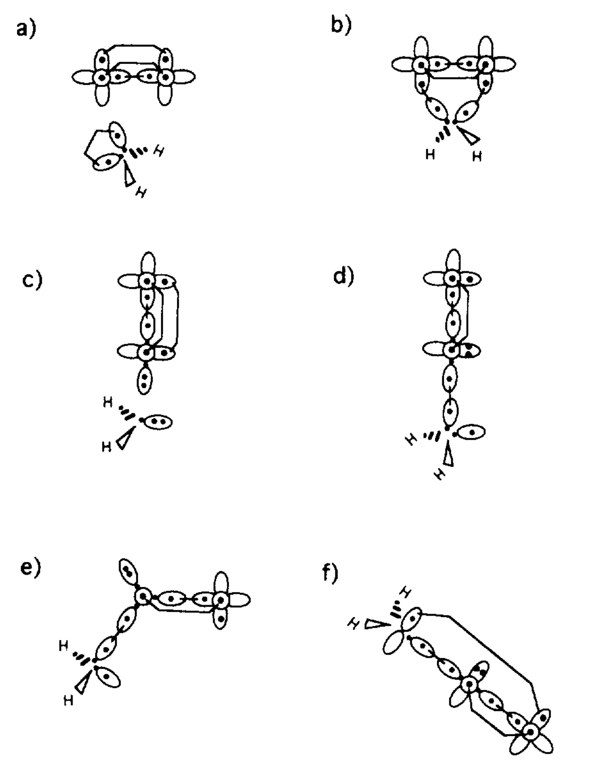

FIG. 1. The electronic structure of selected stationary points on the potential energy surface for $CH_2(^1A_1)+N_2$: (a) sp_1; (b) min 1; (c) sp_3; (d) distorted diazomethane; (e) sp_2; (f) min 2.

TABLE I. Computed energies for stationary points on the $^1CH_2+N_2$ surface.

Geometry	CI1[a]	ΔE[b]
		(a)[c]
Reactants	−148.427 21(−0.469 40)	0.0
min 1	−148.471 56(−0.518 97)	−24.0
min 2	−148.480 05(−0.531 98)	−33.9
$^3CH_2+N_2$	−148.443 88(−0.484 81)	−9.7

Geometry	CI1[a]	ΔE[b]	CI2[a]	ΔE[b]
		(b)[d]		
Reactants	−148.391 06(−0.43026)	0.0	−148.392 69(−0.431 14)	0.0
$^3CH_2+N_2$	−148.408 70(−0.44677)	−10.4		
vdW	−148.390 96(−0.43381)	−0.5		
*sp*3	−148.398 69(−0.44458)	−4.9		
*sp*1	−148.383 37(−0.42918)	4.7	−148.385 66(−0.430 64)	4.4
min 1	−148.434 44(−0.47866)	−23.3	−148.435 68(−0.479 61)	−23.3
*sp*2			−148.359 65(−0.405 59)	19.8
min 2	−148.443 45(−0.49145)	−32.9		−33.2
CH_2N+N			−148.291 37(−0.332 44)	64.3
HCN_2+H	−148.282 39(−0.32161)	66.2		

Geometry	CI1[a]	ΔE[b]
		(c)[e]
Reactants	−148.270 49(−0.29892)	0.0
min 1	−148.311 75(−0.34441)	−21.4
min 2	−148.319 34(−0.35505)	−29.7
$^3CH_2+N_2$	−148.290 72(−0.31842)	−12.3

Geometry	CASSCF	ΔE[a]
		(d)
Reactants	−147.998 52	0.0
*sp*1	−147.967 61	23.5
min 1	−148.015 41	−3.5
*sp*2	−147.939 63	40.8
min 2	−148.011 55	−2.7
vdW	−148.004 30	−1.9
*sp*3	−148.001 51	2.2

[a]The energies are in the form ICCI (ICCI+Q+148).
[b]Relative energies in kcal/mol including zero-point energy (see Table II).
[c]cc-pVQZ basis set.
[d]cc-pVTZ basis set.
[e]cc-pVDZ basis set.

nearly parallel arrangement. This non-least-motion pathway allows the formation of the diazirine molecule [Fig. 1(b)], while maintaining large overlaps between the components of the two bond pairs which change substantially during the course of the reaction (see Ref. 6). By contrast, addition of $^1CH_2$ to N_2 via a C_{2v} pathway requires effectively breaking one bond and is a forbidden process.[7]

Another pathway leading to diazomethane involves initial formation of a dative bond between one N $2s$ lone pair of N_2 and the empty C $2p$ orbital of CH_2 [Fig. 1(c)]. This structure evolves to diazomethane [Fig. 1(d)] by simultaneous donation of the N $2s$ pair onto carbon and back donation of the C $2s$ pair into the π system of diazomethane. This process involves no barrier.

Figure 1(e) shows the orbitals for the saddle point connecting diazirine to diazomethane. The two radical orbitals in Fig. 1(e) arise from the CN σ bond of diazirine which is being broken. The doubly occupied orbital on the center N atom starts as a N $2s$-like lone pair, but becomes sp-like in the saddle-point region and eventually becomes a π orbital for diazomethane. The orbitals for diazomethane are shown in Fig. 1(f). From Fig. 1(f) it is seen that diazomethane has two π electrons in a' orbitals and four π electrons in a'' orbitals (with respect to the molecule plane). The two singly occupied a'' orbitals shown in Fig. 1(f) are singlet paired as a result of through bond coupling from the doubly occupied a'' orbital on the center N.[3]

III. COMPUTATIONAL DETAILS

Several different basis sets were used in these calculations. For the CASSCF derivative calculations, which were used to locate the stationary points, the polarized valence double zeta set of Dunning and Hay[8] was used. The basis sets for C and N are the $(9s5p)/[3s2p]$ basis augmented by a single set of $3d$ functions with exponent 0.75 for C and

TABLE II. Harmonic vibrational frequencies and zero-point energy for $^1CH_2+N_2$. Harmonic frequencies in cm^{-1} obtained from CASSCF calculations with a pVDZ basis set.

*sp*1	vdW	min 1	*sp*2	min 2	CH_2N	HCN_2
Frequencies						
3214	3100	3307	3313	3360	3253	3432
1951	2329	1660	1595	1902	1659	1570
1461	1509	1546	1491	1495	1438	612
1081	534	1033	960	1162	1001	928
477	97	1047	747	560	3360	1251
721*i*	75	836	888*i*	328	1021	891
3348	3176	3436	141	3505		
1009	373	1166	3458	1188		
389	80	1018	1047	419		
ZPE[a]						
0.029 45	0.025 68	0.034 28	0.029 05	0.031 71	0.026 73	0.019 76
*sp*3						
3142						
2342						
1471						
1180						
258						
248*i*						
3240						
1084						
232						
ZPE[a]						
0.029 50						

[a]Zero-point energy in E_H. The zero-point energy for the reactants is 0.022 97.

0.80 for N (pVDZ). The H basis is $(4s)/[2s]$ augmented with a single set of $2p$ functions with exponent 1.00. The basis sets used in ICCI calculations are the Dunning correlation consistent cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets.[9]

The calculations were carried out in C_s symmetry with the mirror plane in the plane of the paper of Fig. 1. The active space for the CASSCF calculations included the eight electrons which are depicted in Fig. 1(a). This required six active orbitals of a' symmetry and two active orbitals of a'' symmetry. The resulting CASSCF calculation had eight electrons distributed among eight orbitals.

The CASSCF gradient calculations used the SIRIUS/ABACUS system of programs,[10] while the ICCI calculations were carried out with MOLPRO.[11,12] All electrons were correlated except for the C $1s$ and N $1s$ like electrons with the restriction that no more than two electrons were allowed into certain weakly occupied orbitals. These orbitals were the highest three a' and highest a'' orbitals for the calculation denoted by CI1 and the highest two a' and highest a'' orbitals for the calculation denoted by CI2. A multireference analog of the Davidson's correction[13] was added to the ICCI energies and is denoted by $+Q$.

IV. DISCUSSION

The computed ICCI energies obtained at the optimized CASSCF geometries are given in Tables I(a), I(b), and I(c) for results obtained with the cc-pVQZ, cc-pVTZ, and cc-pVDZ basis sets, respectively. The zero-point effects were estimated as 1/2 the sum of the harmonic frequencies, which are given in Table II, and the zero-point effects are included in the relative energies, which are also given in Tables I(a)–I(c). Thus, the relative energies are appropriate for comparison to experimental results corrected to 0 K. The relative energies from Table I are also shown in Fig. 2. Table III gives the values of selected bond lengths and angles for the stationary points obtained here and also gives results from

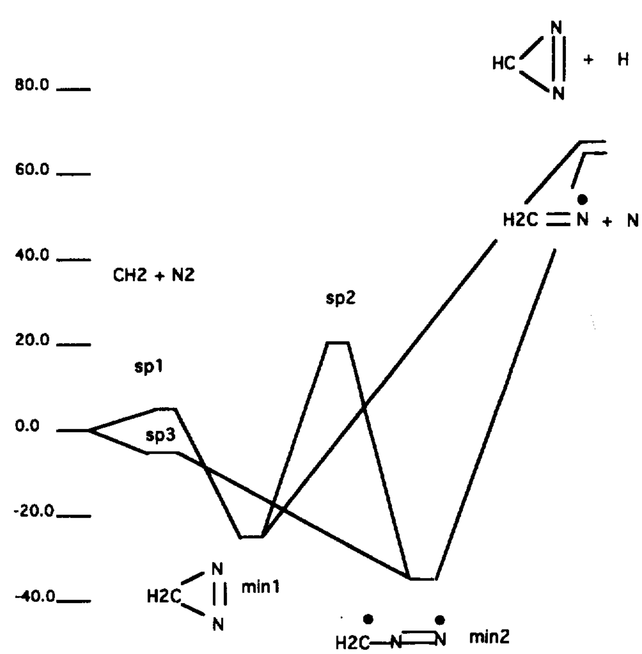

FIG. 2. Computed energetics for the reaction of $CH_2(^1A_1)$ with N_2. Note that while *sp*3 is a saddle point at the CASSCF level, it is below the reactants energy at the ICCI level and it is probable that there is no barrier on this pathway.

TABLE III. Selected bond distances and angles for stationary points.

Structure	r(N–N)	r(N–C)	r(C–H)	∠NNC	∠NCH	∠HCH
			vdW			
CAS/pVDZ[a]	1.121	2.743	1.109	152.4	86.2	102.6
			$sp1$			
CAS/pVDZ[a]	1.158	1.843	1.093	84.2	105.3	110.8
			min 1 (diazirine)			
MP2/6-31G*[b]	1.256	1.480	1.083	64.9	117.2	119.4
SCF/3-21G*[c]	1.188	1.472	1.070	65.9	118.1	
CAS/pVDZ[a]	1.253	1.497	1.081	65.3	117.2	119.7
			$sp2$			
SCF/3-21G*[c]	1.128	1.408	1.068	99.5	116.8	
CAS/pVDZ[a]	1.230	1.488	1.081	109.6	114.2	120.9
			min 2 (diazomethane)			
MP2/6-31G*[b]	1.150	1.311	1.077	178.6	116.9	125.0
SCF/3-21G*[c]	1.110	1.293	1.066	180.0	118.4	123.2
CAS/pVDZ[a]	1.150	1.320	1.076	176.3	116.4	125.1
			$sp3$			
CAS/pVDZ[a]	1.118	1.850	1.101	167.2	93.1	105.5
			$CH_2 \cdot N_2(ts_1)$			
MP2/6-31G*[b]	1.078	1.810	1.091	163.4	93.9	105.4
			$CH_2 \cdot N_2(ts_2)$			
MP2/6-31G*[b]	1.111	1.905	1.076	66.1	90.5	114.8

[a]Present work.
[b]BSHTK, Ref. 4.
[c]GKGBP, Ref. 5.

the work of BSHTK (Ref. 4) and GKGBP (Ref. 5) for comparison. Table IV gives the Cartesian coordinates for the CASSCF optimized structures.

As discussed in Sec. II, $^1CH_2$ plus N_2 can lead to diazomethane via a pathway involving initial formation of a dative bond or to diazirine by addition to the N_2 π bond. The pathway leading to diazomethane involves no barrier (*vide infra*), while the pathway leading to diazirine involves a barrier of 4 kcal/mol. Diazirine is computed to be about 24 kcal/mol below $^1CH_2$ plus N_2. Rearrangement to diazomethane, which is computed to be about 34 kcal/mol below $^1CH_2$ plus N_2, involves a 20 kcal/mol barrier, with respect to reactants (see Fig. 2).

The stationary point structures for diazirine (min 1), diazomethane (min 2), and for the van der Waals minimum (vDW) between $^1CH_2+N_2$, as well as the saddle point structures for the addition of $^1CH_2$ to N_2 to give diazomethane ($sp3$) and diazirine ($sp1$) and the saddle point for rearrangement of diazirine to diazomethane ($sp2$) are shown in Fig. 3. All of these structures are found to be of C_s symmetry. From Table II it is seen that the minima have all real frequencies and the saddle points have only one imaginary frequency, which is of a' symmetry. The HCN_2 structure is taken from the work of Ref. 1. From Table III it is seen that in the van der Waals structure the C–N distance is 2.7 Å and the N_2 is approximately perpendicular to the plane of the CH_2 (∠NCH=86.2). As discussed in Sec. II, this structure may be thought of as a datively bonded structure in which one of the N $2s$ lone pairs of the N_2 donates into the empty $2p$ orbital of the CH_2. Including zero-point energy, the vDW structure is bound by 0.5 kcal/mol with respect to $^1CH_2+N_2$ [see Table I(b)].

Table III also compares the structures obtained here to those obtained by BSHTK (Ref. 4) and GKGBP (Ref. 5). The structures obtained here for diazirine and diazomethane are in good agreement with those obtained by BSHTK at the MP2/6-31G* level. One interesting result is that diazomethane is found to be slightly distorted from C_{2v} symmetry. ∠NNC=176.3 in our calculations compared to 178.6 for BSHTK. The agreement with the results of GKGBP is not as good, but these calculations are only SCF/3-21G*. BSHTK did find a saddle point for conversion of diazomethane to diazirine which is qualitatively the same as our $sp2$.

Table III also shows two saddle-point structures $CH_2 \cdot N_2(ts_1)$ and $CH_2 \cdot N_2(ts_2)$ from BSHTK.[4] $CH_2 \cdot N_2(ts_1)$ is the same as our $sp3$. This saddle-point connects between the van der Waals minimum and diazomethane. From Table III it is seen that there is good agreement between the CASSCF saddle-point structure obtained here and the MP2 results of BSHTK. $CH_2 \cdot N_2(ts2)$ is analogous to our $sp2$ structure. From Table III it is seen that the geometry obtained by BSHTK is qualitatively similar.

The reaction pathways were characterized by following the gradient downhill in both directions away from saddle points $sp1$, $sp2$, and $sp3$. In each case the walk away from the saddle point was started by displacing the geometry by 0.01 times the normal mode corresponding to the negative eigenvalue of the Hessian matrix. The geometries along the

TABLE IV. Cartesian coordinates (in a.u.) for the stationary points of $^1CH_2+N_2$.

	X	Y	Z
		Reactants	
HA	20.000 000	1.636 348	1.317 277
HB	20.000 000	−1.636 348	1.317 277
C	20.000 000	0.000 000	0.005 815
NA	0.000 000	0.000 000	−1.061 015
NB	0.000 000	0.000 000	1.061 015
		vdW	
HA	−1.386 720	1.635 625	−0.254 811
HB	−1.386 720	−1.635 625	−0.254 811
CA	−0.099 095	0.000 000	−0.495 841
NA	0.152 338	0.000 000	4.681 562
NB	0.792 197	0.000 000	6.700 902
		*sp*1	
HA	3.306 430	1.700 893	1.287 566
HB	3.306 430	−1.700 893	1.287 566
C	3.156 047	0.000 000	0.124 535
NA	−0.108 921	0.000 000	−1.088 710
NB	−0.659 985	0.000 000	1.029 043
		min 1	
HA	3.361 487	1.765 350	1.022 398
HB	3.361 487	−1.765 350	1.002 398
C	2.382 992	0.000 000	0.713 766
NA	0.288 198	0.000 000	−1.188 559
NB	−0.424 164	0.000 000	1.069 997
		*sp*2	
HA	3.422 894	1.777 934	0.944 009
HB	3.422 894	−1.777 934	0.944 009
C	2.421 472	0.000 000	0.837 716
NA	0.262 080	0.000 000	−0.963 517
NB	−1.739 341	0.000 000	0.217 783
		min 2	
HA	3.497 594	1.804 588	0.792 830
HB	3.497 594	−1.804 588	0.792 830
C	2.560 109	0.000 000	0.768 062
NA	0.171 030	0.000 000	0.052 381
NB	−1.946 326	0.000 000	−0.436 103
		*sp*3	
CA	−0.051 454	0.000 000	0.055 355
HA	−1.309 639	1.656 983	−0.006 625
HB	−1.309 639	−1.656 983	−0.006 625
NA	0.090 380 9	0.000 000	3.548 880
NB	0.640 351 9	0.000 000	5.589 015
		CH_2N	
HA	0.000 000	1.774 754	−1.038 946
HB	0.000 000	−1.774 754	−1.038 946
C	0.000 000	0.000 000	0.001 129
NA	0.000 000	0.000 000	2.434 016

walk for the pathway connecting $^1CH_2+N_2$ to diazirine via *sp*1, the pathway connecting diazirine to diazomethane via *sp*2, and the pathway connecting $^1CH_2+N_2$ to diazomethane via *sp*3 are shown in Figs. 4, 5, and 6, respectively. The Cartesian coordinates for the geometries at each step along these pathways are given in the appendix (PAPS, Ref. 14).

From Table I(b) it is seen that *sp*3 is below the reactants energy, while the CASSCF energy for *sp*3 is above the CASSCF energy of the reactants. This is interpreted to indicate that the pathway to diazomethane via *sp*3 involves no barrier. This zero barrier path to diazomethane is consistent with the studies by Milligen and Jacox[15] of the products of vacuum-ultraviolet photolysis of methane in an N_2 matrix. These authors report the formation of diazomethane even at 14 K.

Tables I(a)–I(c) give the energetics obtained from the ICCI+Q calculations using the cc-pVQZ, cc-pVTZ, and the cc-pVDZ basis sets, respectively. The binding energies for diazirine and diazomethane with respect to $^1CH_2+N_2$ were estimated by extrapolating the values obtained for the cc-pVDZ, cc-pVTZ, and the cc-pVQZ, basis sets to the basis set limit using the formula given by Woon.[16] The resulting C–N bond dissociation energies are 24.4 kcal/mol for diaz-

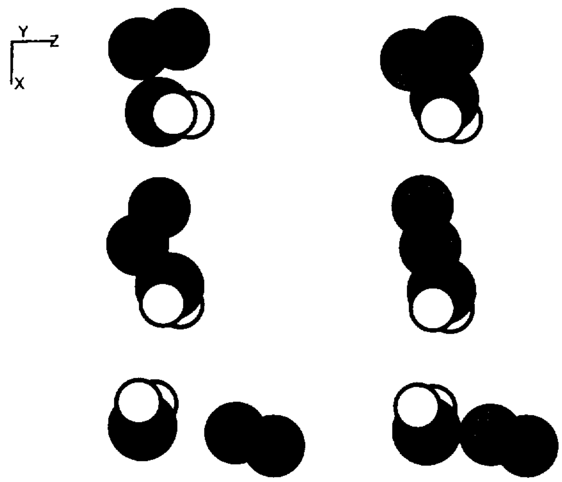

FIG. 3. Geometries for the stationary points on the $^1CH_2+N_2$ surface. Upper left sp_1; upper-right min 1; center left sp_2; center right min 2; bottom left vdW; bottom-right sp_3.

omethane and 34.1 kcal/mol for diazirine. These values include zero-point effects and are appropriate for 0 K. Using a heat of formation of $^1CH_2$ of 102.1 kcal/mol obtained from the heat of formation of $^3CH_2$ of 93 kcal/mol and a singlet-triplet splitting of 9.1 kcal/mol gives heats of formation of 77.7 kcal/mol for diazirine and 68.0 kcal/mol for diazomethane. Laufer and Okobe[17] report the heat of formation of diazirine as 60.6–66 kcal/mol. However, there is an earlier value of 79.3 kcal/mol by Paulett and Ettinger.[18] The discrepancy between our calculated value and the value of Laufer and Okobe is surprisingly large and our calculations support the value obtained by Paulett and Ettinger. Laufer and Okobe also report a heat of formation of 51–60 kcal/mol for diazomethane.[19] This is also surprisingly far from our computed value. Calculations for the D_e of N_2 using the same extrapolation method as used here give an extrapolated value of 226.8 kcal/mol compared to an experimental value of 228.4 kcal/mol.[20] As a further check on the computed results, we also computed the energy of $^3CH_2+N_2$ with each of the basis sets. The $^3CH_2$ geometry was taken from the work of Bauschlicher, Langhoff, and Taylor[21] who carried out a definitive study of the singlet-triplet splitting in CH_2. These results are also given in Tables I(a)–I(c). Here it is seen that the cc-pVQZ basis set gives a separation of 9.7 kcal/mol compared to 9.1 kcal/mol obtained in Ref. 21 with a comparable size ANO basis set. Taking these considerations together leads us to assign a maximum error of 2 kcal/mol to our reported 0 K heats of formation for diazirine and diazomethane.

From Ref. 20 it is expected that the barrier heights obtained with the cc-pVTZ basis set would change by less than 0.5 kcal/mol if extrapolated to the basis set limit. This occurs because the barrier height involves an energy difference between a bond that is being broken and a bond that is forming and therefore there is a cancellation of errors. Accordingly, this extrapolation was not carried out for the barrier heights reported in Table I(b).

Table I(d) gives energetics for the stationary points obtained at the CASSCF level with the pVDZ basis set. As expected, these energetics are much less reliable than those obtained from the ICCI calculations. The general trends are that the binding energies are underestimated and the barrier heights are overestimated. In spite of these obvious defects in the CASSCF energetics, comparison of CASSCF and ICCI stationary points for the $N+O_2$ reaction[22] showed that the CASSCF method does a very good job of predicting the geometry in the directions perpendicular to the reaction coordinate, but that the saddle-point geometries can be shifted somewhat along the direction of the reaction coordinate. An

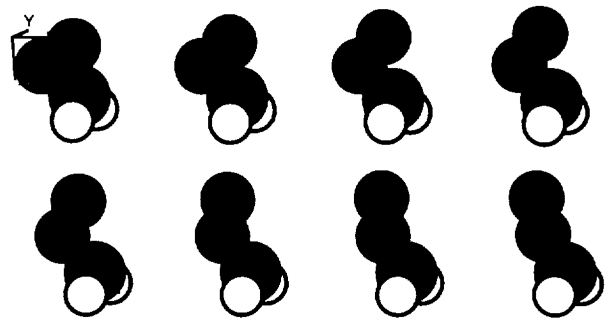

FIG. 5. Geometries along the reaction path connecting diazirine with diazomethane.

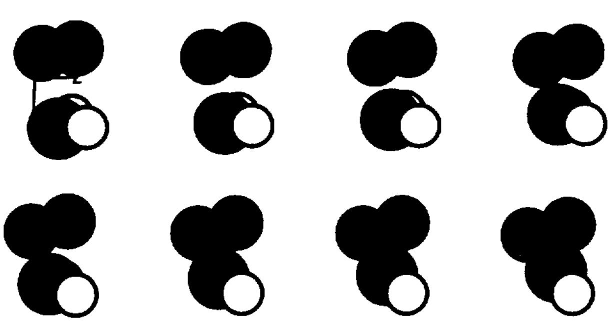

FIG. 4. Geometries along the reaction path connecting $^1CH_2+N_2$ with diazirine.

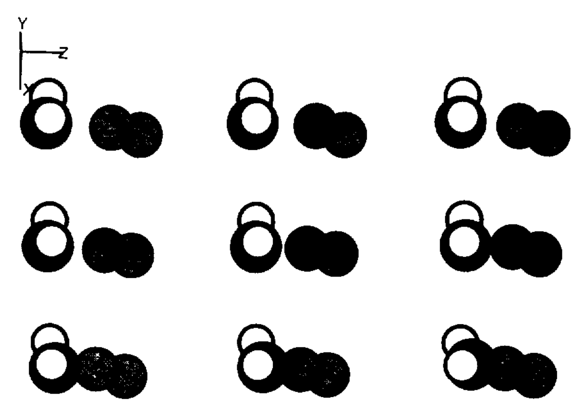

FIG. 6. Geometries along the reaction path connecting $^1CH_2+N_2$ with diazomethane.

extreme example of this effect, in the present calculations, occurs for *sp*3, where the ICCI method finds an energy at the saddle-point geometry below that of the reactants. This has been interpreted to mean that the barrier is shifted far out into the entrance channel and in fact there is probably no barrier. In a case where the barrier persists at the ICCI level, the shift along the reaction coordinate is normally much less significant.

We now return to consideration of other product channels in the reaction of $^1CH_2$ with N_2. Formation of CH_2N+N is endothermic by 64 kcal/mol and involves a singlet-triplet crossing. Thus, this pathway is not a likely product channel. Dissociation of diazirine to CHN_2+H can lead to either doublet or quartet CHN_2. The quartet state (*q* min 1 of Ref. 1) is 17.0 kcal/mol above the doublet state (*d* min 2). However, CHN_2+H is computed to be endothermic by 66 kcal/mol, with respect to reactants, for the doublet state of CHN_2, and is also not a likely direct product.

More likely processes leading to CHN_2 are hydrogen abstraction from diazirine or diazomethane, both of which are expected to be important products of the reaction of $^1CH_2$ with N_2. Hydrogen abstraction from diazomethane leads to an HCN_2 geometry like the dative structure of Manaa and Yarkony.[23] Previous theoretical studies[1] indicate that there is a large barrier between the dative structure and the region of the surface leading to HCN+N. Thus, this pathway is not expected to contribute to prompt NO formation. On the other hand, hydrogen abstraction from diazirine leads to an HCN_2 geometry like that involved in the doublet-quartet surface crossing region of the $CH+N_2$ surface. For example, the reaction

$$\text{diazirine}+OH \rightarrow CHN_2+H_2O \tag{1}$$

is exothermic by 28.5 kcal/mol. In addition, assuming no vibrational relaxation, diazirine formed from $^1CH_2+N_2$ would have about 38 kcal/mol of internal energy (energy of sp_1 minus energy of min 2), leading to a total of 66 kcal/mol of available energy. As the NN bond is considerably shorter in diazirine it is probable that CHN_2 will be formed with a large amount of energy in the NN stretching mode. [The quartet state of CHN_2 has a longer NN bond (2.377 Å) than the doublet state (1.635 Å), which in turn is longer than the NN bond in diazirine (1.253 Å).] From Ref. 1 the saddle points leading to $CH+N_2$ on the doublet surface and to HCN+N on the quartet surface are 31 kcal/mol and 36 kcal/mol above *d* min 2, respectively. Thus, if this much energy is transfered into vibrational energy, these channels are energetically accessible. Furthermore, energy in the NN stretching mode also favors the doublet to quartet crossing [In Eq. (1) the CHN2 is formed initially in the doublet state], leading to $HCN+N(^4S)$, as for the $CH(^2\Pi)+N_2$ reaction.

V. CONCLUSIONS

The reaction pathways for the reaction of $^1CH_2$ with N_2 have been studied using complete active space self-consistent field (CASSCF) derivative methods to characterize the stationary points and internally contacted configuration interaction (ICCI) to determine the energetics. $^1CH_2+N_2$ can lead to diazomethane, with no barrier, or to diazirine, with a barrier of 5 kcal/mol. Diazirine is computed to be about 24 kcal/mol below $^1CH_2$ plus N_2. Rearrangement to diazomethane involves a 20 kcal/mol barrier, with respect to reactants, and diazomethane is computed to be about 34 kcal/mol below $^1CH_2$ plus N_2. The CH_2N+N and CHN_2+H channels are computed to be endothermic by 64 kcal/mol and 66 kcal/mol, respectively. Thus, these product channels are unlikely to be important.

The computed potential energy surface would suggest that diazirine will be readily formed from $^1CH_2$ plus N_2. It is proposed that subsequent reaction of diazirine with hydrogen abstracters such as OH, which would be abundant in the combustion environment, would lead to doublet CHN_2, with considerable vibrational excitation, especially in the NN stretch mode, which would facilitate doublet to quartet crossing, leading to HCN+N product. Thus, this pathway may be an important new source of "prompt" NO.

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[1] S. P. Walch, Chem. Phys. Lett. **208**, 214 (1993).
[2] J. A. Miller and C. T. Bowman, Progr. Energy Combustion Sci. **15**, 287 (1989).
[3] S. P. Walch and W. A. Goddard III, J. Am. Chem. Soc. **97**, 5319 (1975).
[4] A. I. Boldyrev, P. R. Schleyer, D. Higgins, C. Thomson, and S. S. Kramarenko, J. Comp. Chem. **13**, 1066 (1992).
[5] C. Guimon, S. Khayar, F. Gracian, M. Begtrup, and G. Pfister-Guillouzo, Chem. Phys. **138**, 157 (1989).
[6] T. H. Dunning, Jr. and L. B. Harding, in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC Press, Boca Raton, 1985), pp. 1–69.
[7] W. A. Goddard III, J. Am. Chem. Soc. **94**, 793 (1972).
[8] T. H. Dunning, Jr., and P. J. Hay, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer, III (Plenum, New York, 1977).
[9] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[10] SIRIUS is an MCSCF program written by H. J. Jensen and H. Agren and ABACUS is an MCSCF derivatives program written by T. Helgaker, H. J. Jensen, P. Jørenson, J. Olsen, and P. R. Taylor.
[11] H.-J. Werner and P. J. Knowles, J. Chem. Phys. **89**, 5803 (1988).
[12] P. J. Knowles and H.-J. Werner, Chem. Phys. Lett. **145**, 514 (1988).
[13] S. R. Langhoff and E. R. Davidson, Intern. J. Quantum Chem. **8**, 61 (1974).
[14] See AIP document no. PAPS JCPSA-103-4930-16 for 16 pages of Tables of Cartesian coordinates. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, Carolyn Gehlbach, 500 Sunnyside Boulevard., Woodbury, New York 11797-2999 Fax: 516-576-2223, e-mail: janis@aip.org. The price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.
[15] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 5146 (1967).
[16] D. E. Woon, Chem. Phys. Lett. **204**, 29 (1993); J. Chem. Phys. **100**, 2838 (1994).
[17] A. H. Laufer and H. Okabe, J. Phys. Chem. **76**, 3504 (1972).
[18] G. S. Paulett and R. Ettinger, J. Chem. Phys. **39**, 825 (1963); **39**, 3534 (1963).
[19] A. H. Laufer and H. Okabe, J. Amer. Chem. Soc. **93**, 4137 (1971).
[20] S. P. Walch and H. Partridge, Chem. Phys. Lett. **223**, 331 (1995).
[21] C. W. Bauschlicher, Jr., S. R. Langhoff, and P. R. Taylor, J. Chem. Phys. **87**, 387 (1987).
[22] S. P. Walch, J. Chem. Phys. **102**, 4189 (1995).
[23] M. R. Manaa and D. R. Yarkony, J. Chem. Phys. **95**, 1808 (1991); Chem. Phys. Lett. **188**, 352 (1992).